Time-Resolved Step-Scan and Rapid-Scan Fourier-Transform Infrared Spectroscopy

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1. Introduction

Infrared spectroscopy has played a major role in the identification of reaction intermediates on solid catalysts since the first IR detection of a surface-adsorbed species fifty years ago [1-7]. The wealth of information on surface intermediates obtained from infrared studies has contributed heavily to the current mechanistic understanding of many heterogeneously catalyzed reactions. The strength of this in-situ technique is that it is capable of furnishing both structural and kinetic information of reaction intermediates on surfaces as well as the surrounding gas or solution phase. Important tools for structural identification of intermediates include isotopic labeling and the use of authentic samples, which generally are readily available. Moreover, the most often used catalyst supports (high-area oxides, zeolites) are transparent over wide regions of the infrared and suitable for use in transmission mode, especially if the catalyst is prepared in the form of a pressed wafer. Alternatively, the diffusion-reflection infrared method can be employed in the case of catalysts in powder form. Thus, considerable portions of the vibrational absorption spectrum of reaction intermediates and final products are accessible for structural and kinetic analysis. For the detection of species adsorbed on model single crystal surfaces, in particular metal surfaces, reflection-absorption infrared spectroscopy (RAIRS or IRAS (IRRAS)) has proven an effective tool even at single monolayer coverage [8-10].

While these infrared methods were developed in the 1950 and 1960 using grating instruments, the advent of commercial Fourier-transform infrared spectrometers in the 1970 resulted in a several orders of magnitude increase of the sensitivity. The dramatically enhanced sensitivity of the FT-IR method over grating-based techniques for uncovering reaction intermediates on catalyst surfaces is not only due to the familiar multiplex and throughput advantage [11], but also to the much more accurate way of computing reaction difference spectra. The achievements of static (non time-resolved) infrared spectroscopy for monitoring heterogeneous catalysis is reviewed comprehensively in this book by Thibault-Starzyk and Lavalley, and in the chapter of Buergi and Baiker.

In-situ monitoring of catalytic reactions by static (i.e. continuous scan) FT-IR spectroscopy affords the detection and structural characterization of intermediates, but it is difficult, and often impossible, to determine the mechanistic role of the observed species in the absence of information on the temporal behavior. Knowledge of the rate of reaction of surface intermediates and the relationship to final product buildup is required for assessing whether or not the species are kinetically relevant. Moreover, the lifetime of intermediates under reaction conditions is often very short, which prevents buildup of the steady-state concentrations needed for detection by static FT-IR spectroscopy. Initiation of reaction by short pulses synchronized with time-resolved infrared monitoring is required to detect and determine the reactivity of intermediates that remain elusive under steady-state conditions. Time-resolved FT-IR techniques are ideal for this purpose because they benefit from all the advantages already exploited in static FT-IR studies. For the time scale of 10 milliseconds and slower, rapid-scan FT-IR spectroscopy is the method of choice, which has been available in commercial instruments since 20 years [12]. For FT-IR monitoring in the time range from 10 nanoseconds to milliseconds, the step-scan technique is most suitable. While proposed as early as 1980 [13,14], instrumentation that allows to make use of the method has only recently been developed.

After a brief review of technical aspects of time-resolved FT-IR spectroscopy (Section 2), we will focus on recent continuous and rapid-scan FT-IR studies on the second and millisecond time scale in which catalysis is initiated by pulsed release of a reactant. While the time resolution is modest, the work illustrates the need for time-resolved measurements in order to capture intermediates of heterogeneous catalysis that would otherwise escape detection and to determine their kinetic significance (Section 3). This will be followed in Section 4 by case studies from our laboratory on the monitoring of radicals and closed-shell intermediates on microporous supports by step-scan FT-IR spectroscopy on the microsecond and nanosecond time scale.

2. Technical Aspects of Time-Resolved FT-IR Spectroscopy

2.1 Rapid-Scan Method

The rapid-scan method affords FT-IR spectra in the millisecond and second time range, with a limit of about 10 milliseconds on modern FT-IR instruments. The technique, which has been available since the arrival of commercial FT-IR spectrometers in the 1970 is based on the same measurement principles employed for recording conventional static FT-IR spectra [12].

The crucial additional feature is the triggering of chemical reaction synchronous with the recording of interferograms. Such triggering can be accomplished by excitation of a reactant with a visible or UV light pulse, or by release of a reactant by photodissociation of a precursor, or simply through a mechanical valve that can be opened and closed on the micro or millisecond time scale. When using the method in its simplest form as schematically illustrated in figure 1, chemical reaction is triggered by a signal that is precisely timed with respect to the motion of the moving interferometer mirror. For example, initiation of reaction can coincide with the start of a forward motion of the mirror. A pre-determined number of interferograms is then recorded, symbolized by squares labeled 1.1, 1.2, 1.3 etc. in figure 1 (bottom row). The underlying assumption of the method is that the duration of each interferogram (10 milliseconds or longer) is short compared to time scale of the kinetic processes of interest [12]. Once chemical change has ceased (interferogram 1.7 in our example), the reaction is triggered again synchronously with a forward motion of the mirror and interferograms are collected according to the same protocol as before (second row from bottom in figure 1). The experiment is repeated, typically tens of times in order to furnish sufficient data for signal averaging. There is great flexibility in the choice of the length of the interferograms, which is tied to the spectral and temporal resolution, and the number of interferograms recorded between reaction initiation pulses. The latter is determined by the time scale of the chemical process of interest. Moreover, software manipulations permit instant averaging of consecutive interferograms during data acquisition, which is very useful if there are time intervals of no interest for the process under study. This is illustrated in figure 1 by the entry 1.6, which represents the average of four consecutive interferograms. Such averaging during data acquisition makes subsequent data manipulation less cumbersome, which involves Fourier transformation of the entire “matrix” of interferograms

(50x7 = 350 in the case of the example shown in figure 1). Subsequent ratioing of spectra of a given row, or of spectra of adjacent rows furnishes kinetic information on reaction intermediates and the growth of final products, as will be illustrated by case studies discussed below.

2.2 Step-Scan Method

The step-scan method recently implemented in commercial FT-IR instruments affords spectra on a much faster time scale, with a limit of about 10 nanoseconds. The technique was first proposed by Sakai and Murphy over 20 years ago [13,14], but its realization had to await progress in the development of interferometer electronics, fast digitizers, and infrared photon detectors with nanosecond response time. In step-scan FT-IR spectroscopy, the time course of the interferometric signal is recorded while holding the movable mirror fixed at each position along the mirror path. After the mirror has settled at a given position, a chemical reaction is initiated and the growth and decay of transients is measured and digitized, as illustrated schematically in figure 2. Typically, tens of decays are recorded and averaged for signal improvement. For triggering of chemical reaction on the nano or microsecond time scale, a light pulse is required. The photons initiate reaction either by direct excitation of a reactant, or by fast release of a reactant from a photo-labile precursor. After moving the mirror to the next position, reaction is again initiated and the temporal behavior recorded. This process is repeated until the mirror has stepped through all positions required for the desired spectral resolution and frequency range. From this set of decay curves, an interferogram for each time delay with respect to start of reaction is computed. Fourier transformation furnishes a single beam infrared spectrum for each time point. Simple in concept, the technique is only limited by the response time and detection limit of the infrared detector, the bandwidth of the data acquisition electronics, and the stability of the stepping mirror, all of which can be improved as progress is made in the technology of these components. It eliminates the restriction on time resolution and the tendency for artifacts of the earlier stroboscopic techniques for recording FT-IR spectra at sub-millisecond resolution [12,15,16].

While a few groups began to use the step-scan method for transient absorption experiments on the microsecond time scale already in the early 1990 [17-21], and for emission studies in the nanosecond regime around the same time [22], measurements in the absorption mode at 10 nanosecond resolution required further hardware and software modifications in order to reach sufficient sensitivity. One crucial requirement for transient absorption measurements in the nanosecond regime is recording of the reaction-induced change of the interferometer signal while suppressing the orders of magnitude larger, static signal. Hence, nanosecond response time detectors are needed that afford simultaneous recording of the AC-coupled and DC-coupled infrared interferometric signal (the DC interferogram is needed for determination of the phase correction upon Fourier transformation of the AC interferogram). Hardware and software modifications on a commercial FT-IR instrument in collaboration with Bruker engineers allowed us to achieve sensitive transient step-scan FT-IR spectroscopy at 10 nanosecond resolution, as demonstrated by monitoring photoisomerization processes of biomolecules [23,24], recording of infrared spectra of triplet excited organics in a zeolite [25], or of chemical reactions in solution under flow conditions [26,27].

3. FT-IR Monitoring of Catalysis Under Pulsed Reactant Release

In the past ten years, several research groups have begun to push the time resolution of FT-IR spectroscopy of processes on solid catalysts into the second and millisecond regime by pulsed release of reactants coupled with monitoring by the rapid-scan technique. Example include reactions at the gas-solid interface of supported catalysts (Rh-SiO_2, Rh-Al_2O_3, Pt-SiO_2) [28-31], and cation-exchanged or framework zeolites [32-35]. Moreover, rapid-scan FT-IR spectroscopy in grazing incidence configuration, sometimes coupled with pulsed molecular beams has been used to monitor the dynamics of adsorbed species on single crystal surfaces [36-42]. We illustrate here the type of new mechanistic insight revealed by infrared monitoring on the second and millisecond time scale by two examples, namely the study of a reaction on a supported metal catalyst, and in a cation-exchanged zeolite.

3.1 Transient Surface Intermediate on Oxide-Supported Metal Catalyst

Using a fast mechanical valve to generate short pulses of reactants, Chuang and coworkers monitored the fate of surface intermediates of the reaction of NO with CO gas over a silica-supported Rh catalyst by in-situ FT-IR spectroscopy on the time scale of seconds [28,43-45]. The reaction is of practical importance in the removal of pollutants from combustion exhausts. Figure 3 shows the evolution of infrared spectra following release of a 10 cm^3 pulse of NO gas into a steady flow of CO (10 cm^3min^{-1}, in 30 cm^3min^{-1} He) over a pressed disk of Rh-SiO_2 catalyst at 473 K [43]. Since the NO gas pulse released by the valve requires 40 sec to reach the catalyst, the traces t=0 and t=33 sec show only the gaseous CO band centered at 2140 cm^{-1} and a linear RhCO surface species absorbing at 2056 cm^{-1}. As can be seen from figure 3, the next following spectral trace (t=43 sec) confirms the arrival of NO by its gas phase absorption centered at 1870 cm^{-1}. Reaction is signaled by the appearance of a surface RhNO species at 1642 cm^{-1} at the expense of RhCO, and the formation of some N_2O (2240 and 2201 cm^{-1}).

The interesting observation is the increase of the RhNO species up to about 60 sec and the subsequent decrease under concurrent growth of the $Rh(CO)_2^+$ complex, with absorptions at 2032 and 2090 cm^{-1}. At the same time, gaseous CO_2 is produced. This shows that RhNO is a reaction intermediate. The depletion of RhNO is attributed to decomposition to RhN (which is the source of N_2O upon reaction with NO) and surface oxide under oxidation of Rh atoms. The latter is the rate-limiting step of the reaction. Rh^+ so formed is known to bind CO molecules to yield $Rh(CO)_2^+$ species [43], the sites at which CO reacts rapidly with surface oxygen to produce CO_2. In a separate experiment in which the ^{12}CO flow was rapidly switched to ^{13}CO flow during a steady-state NO + CO reaction, it was found that the $RhN^{12}CO$ response lagged behind the $^{12}CO_2 \rightarrow {}^{13}CO_2$ response [45]. Hence, the isocyanate species is ruled out as a reaction intermediate of CO_2 production. These pulsed experiments coupled with FT-IR monitoring on the still relatively slow time scale of seconds reveal the kinetic significance of reaction intermediates, which is not accessible by steady-state methods [44,46,47]. Clearly, the development of FT-IR methods that allow the detection and kinetic evaluation of transients on shorter time scales are expected to lead to a new level of insight into the mechanism of heterogeneous catalysis.

3.2 Millisecond FT-IR Spectroscopy of Reactant Exchange at Catalytic Site in a Zeolite

Rapid scan FT-IR spectroscopy at 100 millisec resolution has been employed by Iwamoto and Hoshino for monitoring intermediates upon adsorption of NO gas onto Co^{2+}-exchanged zeolite ZSM-5 [32]. Cobalt–exchanged zeolites are highly active for the reduction of undesirable NO_x effluents by hydrocarbons [48]. The dominant adsorption site of NO is a Co^{2+} dinitrosyl species [49] characterized by symmetric (1858 cm^{-1}) and asymmetric NO stretching absorptions (1776 cm^{-1}) shown in trace (a) of figure 4 ($Co(^{15}NO)_2^{2+}$ isotopic modification). The Co^{2+} dinitrosyl complex is indefinitely stable at room temperature [50]. However, exposure of an evacuated $Co(^{15}NO)_2{}^{2+}$ - ZSM-5 sample to 13 Torr of ^{14}NO gas results in exchange of NO ligands at the Co^{2+} site on the hundreds of millisec time scale. Traces b-e of figure 4, recorded in the time window between 300 and 700 msec after ^{14}NO release indicate rapid loss of $Co(^{15}NO)_2^{2+}$ under formation of a mixed isotope $Co(^{15}NO)(^{14}NO)^{2+}$ intermediate, absorbing at 1882 and 1790 cm^{-1}. The intermediate disappears within about 2 sec while fully exchanged $Co(^{14}NO)_2^{2+}$ grows in (1894 and 1810 cm^{-1}). This study reveals for the first time that NO ligands are exchanged one by one at the Co^{2+} dinitrosyl site, reaching rapidly an equilibrium with gas phase NO. The authors speculate that a short-lived trinitrosyl intermediate may precede the mono-exchanged Co dinitrosyl intermediate, observation of which would require sub-millisec resolution. Furthermore, a minor site, $Co(^{15}NO)^{2+}$ absorbing at 1904 cm^{-1} is seen to completely disappear within 300 msec of ^{14}NO exposure and be replaced by $Co(^{14}NO)^{2+}$ at 1942 cm^{-1}. This confirms that the mononitrosyl site is much more labile than the Co^{2+} dinitrosyl species, thus furnishing a direct kinetic insight made possible only by monitoring in a time-resolved mode.

4. Monitoring of Transient Radicals and Intermediates by Step-Scan FT-IR Spectroscopy

The monitoring of primary steps of heterogeneous catalysis under reaction conditions by time-resolved FT-IR spectroscopy may typically require a time resolution much better than milliseconds. The behavior of short-lived species like surface intermediates on metal particles, mobile radicals on supports, or transient complexes often determines the final product distribution of a catalytic reaction. Hence, improvement of the selectivity of heterogeneous catalysis is closely tied to controlling the fate of short-lived intermediates, which requires methods to detect and structurally characterize such species. Equally important is monitoring of the kinetics, which may require access to the entire time range from ultrafast to milliseconds. The step-scan FT-IR method covers a large fraction of this time span from 10 nanoseconds to milliseconds. We have addressed in the past few years the technical challenges of detecting and monitoring in real time small transient radicals and closed-shell intermediates on zeolite and other microporous supports by this method. Zeolites play a central role as catalysts in the petrochemical and, increasingly, in the fine chemicals industry [51-53]. Recent advances will be described by two case studies.

4.1 Detection of Small Transient Radicals on Zeolite Supports

To detect radical intermediates by FT-IR spectroscopy, one has to be able to trigger the catalytic reaction fast on the time scale of interest, yet generate the chemical intermediates in sufficiently high concentration so that FT-IR detection is feasible. A well-established method for producing intermediates in a concerted fashion in a short period of time is initiation by a laser photolysis pulse. This can involve activation of a reactant with a visible or UV light pulse, or release of a reactant by photodissociation of a precursor, as already described in Sect. 2. For monitoring of processes on the hundreds of microsecond time scale, release of a reactant through a mechanical valve that opens and closes on that time scale may be used. A further technical challenge is the requirement for pulse-to-pulse repeatability of the chemical process in a step-scan experiment; typically, tens of thousands of pulses are needed for a single step-scan run. This condition is readily fulfilled for reversible photophysical processes, like recording of the triplet-excited state FT-IR of an organic molecule in a zeolite [25]. Chemical reaction monitored in conjunction with a flow system, with the irradicated solution volume completely replaced between excitation pulses, also results in highly reproducible sample conditions from pulse to pulse [26,27]. However, flow systems at the fast rates required for sample replacement between photolysis pulses are not practical in the case of 3-dimensional porous catalyst supports. As in any static sample, reactant depletion and final product buildup are unavoidable. Therefore, the applicability of step-scan FT-IR spectroscopy for the monitoring of irreversible reactions in a zeolite had first to be explored. Our approach consists of exploiting the capacity of molecular sieves for adsorbing a large reservoir of reactants, while converting only a small fraction during a given step-scan run. In this way, the reaction proceeds in a regime of almost negligible reactant depletion.

Small acyl radicals like formyl or acetyl radical are proposed intermediates of a number of catalytic processes on heterogeneous supports [54], including zeolites [55]. Since these radicals have intense infrared C=O stretch absorptions in a spectral region free of most other molecular vibrations, generation of HCO or CH_3CO inside zeolite pores offers the best chance for detecting such species by step-scan FT-IR spectroscopy. The studies promise to furnish a first look at lifetime and kinetic behavior of small radicals in a microporous environment.

4.1.1 Transient HCO Radical in Zeolite NaY

Formyl radicals are known to be efficiently generated in the gas phase or solution by photodissociation of small aldehydes like acetaldehyde [56] or glycolaldehyde [57]. We have attempted to produce the radicals in cation-exchanged zeolite Y, an aluminosilicate sieve (Si:Al=2.4) of industrial importance. The zeolite consists of a three-dimensional network of large spherical cages called supercages (13Å diameter) [58]. As shown in figure 5, these are interconnected by 8Å diameter windows (four per cage) that allow facile cage-to-cage passage of small and medium-size molecules. The static FT-IR spectrum recorded upon loading of a self-supported pressed pellet of 1µ NaY crystallites (1 cm diameter, 50-100µ thick) with glycolaldehyde gas, shown in figure 6a confirmed that the precursor is adsorbed as a monomeric species. Irradiation with 266 mm light resulted in very efficient conversion of the aldehyde to CH_3OH (1353, 1455, 1471, 2850, 2958, 3400 cm^{-1}), CO gas (gas phase rotation-vibration bands in the 2000-2200 cm^{-1} region), $CH_2{=}O$ (1505 cm^{-1}), and HCO_2^- (1606 cm^{-1}) as shown in the photolysis difference spectrum figure 6b and, in more detail in figure 7 [59]. As can be seen from figure 8, these stable products are all readily explained by a single fragmentation path, namely dissociation to formyl radical and hydroxymethyl radical. This suggests that glycolaldehyde is a clean and efficient photolytic source of formyl radicals in a zeolite.

Step-scan FT-IR runs at 5μsec resolution using 266 nm laser photolysis pulses of 8 nsec duration revealed a transient absorption at 1847 cm^{-1}, shown in figure 9a. The band is close to the CO stretching frequency of gas phase HCO radical at 1868 cm^{-1} [60]. The signal of $5x10^{-5}$ absorbance units (peak height) corresponds to a total of about 10^{-10} mol of HCO radicals in the zeolite wafer volume. A similar study using acetaldehyde precursor in NaY showed the same transient absorption at 1847 cm^{-1}. As can be seen from figure 10a, ^{13}C isotope labeling of the carbonyl C of acetaldehyde results in a red shift of the transient infrared band by 40 cm^{-1}, confirming the assignment to a C=O group. These experiments with acetaldehyde were conducted with 25 nsec resolution; the spectra of figure 10a represent the coaddition of the 200 slices over the first 5 μsec after the photolysis pulse. Based on the agreement of the transient infrared band detected upon fragmentation of glycolaldehyde and acetaldehyde, we conclude that the 1847 cm^{-1} species is HCO radical.

The decay of HCO radicals in NaY, whether produced from glycolaldehyde (figure 9b) or acetaldehyde precursor (figure 10b) is surprisingly slow and exhibits biphasic kinetics. In the case of glycocaldehyde, the initial decay (0-30 μsec) is well described by a single exponential law

$$A_t = A_o \cdot e^{-k_1 t}$$

with $k_1 = (4.2 \pm 0.5)\ 10^4\ sec^{-1}$, corresponding to a lifetime of 24 μsec. In the case of acetaldehyde precursor, the initial decay time is 20 μsec. On the other hand, the estimated residence time of a triatomic species like HCO in a supercage of zeolite Y is extremely short, namely around one nsec (calculated from the Einstein relation [61] $t = \langle r^2(t)\rangle/6D$ assuming a diffusion coefficient $D = 3\times10^{-10}$ m^2 sec^{-1} equal to that of $CH_2{=}CH_2$, a species of similar shape, size, and degree of unsaturation [62]). Hence, even the fast decay of HCO of about 20 μsec is many orders of magnitude longer than the time it takes for the small radical to hop from cage to cage. Moreover, quantitative estimates confirm that the initial intensity of the 1847 cm^{-1} band accounts within uncertainties for every HCO radical generated by the photolysis pulse [59]. Therefore, the geminate HCO and CH_2OH (or CH_3) radicals separate quantitatively from the supercage in which they are produced and undertake random walks until a reactive encounter occurs. It is surprising that instant radical reaction in the nascent supercage does not take place. It suggests that the availability of facile escape routes through the four large window openings (figure 5), and electrostatic or H-bonding interactions between radicals and extra framework Na^+ ions or the negatively charged walls dramatically reduce the probability of radical recombination in the original supercage.

What does the biphasic kinetics of the HCO decay tell us about the fate of small radicals in an ambient temperature zeolite? The question can best be addressed by the glycolaldehyde experiment because the stable photolysis products, namely CO, CH_3OH, and $CH_2{=}O$ are formed by one or the other of two competing HCO + CH_2OH channels, shown in figure 8 (HCO_2CH_3 and HCO_2^- are secondary thermal reaction products of formaldehyde) [59,63,64]. The total rate of HCO decay is the sum of the rates of the two alternative H-atom transfer paths of HCO + CH_2OH encounters. Hence, the observation of two distinct decay kinetics can only originate from a heterogeneity that influences the total reaction rate. The only possibility we can conceive of is the occurrence of geminate and nongeminate radical reaction. In fact, such a behavior was predicted by computer simulation of the decay of radical pairs assuming random walk in an infinite NaX lattice (isostructural with NaY) [58] by Johnston et al. [65]. The calculations indicate that about half of the geminate radicals do not re-encounter but, rather, undergo nongeminate processes that occur on a much longer time scale. Therefore, we attribute the fast decay with a 1/e time of 24 μsec to the reaction of geminate HCO and CH_2OH radicals that separate from the supercage in which they were generated, but meet again and react before they have an opportunity to escape from the diffusion environment they share. On the other hand, radicals that escape the geminate diffusion environment will ultimately react with a partner of another photolyzed precursor.

The explanation of the biphasic decay kinetics in terms of geminate and nongeminate encounters is supported by estimates of the spatial and temporal aspects of these processes. Based on extinction coefficient estimates [59], we calculate that each photolysis pulse generates $9x10^{15}$ radicals pairs per cm^3. This corresponds to an average separation between photolyzed precursors of 600Å. At the same time, we are able to estimate the extent of the sphere in which geminate HCO and CH_2OH encounters occur because the problem of geminate reaction in a finite subspace of the zeolite crystallite is closely connected with the known problem of the survival of a random walker in a finite 3-dimensional lattice with a single trap [66,67]. Using this model in conjunction with the cage-to-cage hopping time of HCO radicals and the diffusion coefficient in NaY discussed above, we calculate that the radical probes on average $1.8x10^4$ supercages during the 24 μsec geminate reaction time [59]. This corresponds to a sphere with a radius of 200Å [58]. Hence, the time frame of geminate encounters coincides with the time it takes for a radical to approach the diffusion sphere of an adjacent radical pair. This supports our assignment of the fast component of the radical decay to the reaction of geminate HCO + CH_2OH pairs.

On the other hand, nongeminate encounters of the radicals are expected to follow a second-order rate law described by [65]

$$R_t = \frac{R_o}{1 + k_2 t R_o}$$

$$k_2 = 8\pi D\rho$$

R_o is the initial concentration of the radicals that escaped geminate reaction, k_2 is the bimolecular reaction rate constant, D the sum of the diffusion coefficients of HCO and CH_2OH radical in the zeolite, $3.3\text{x}10^{-10}\ m^2 sec^{-1}$, and ρ the reaction radius. The supercage radius of 6Å is taken as the reaction radius [58]. With these values for the parameters, k_2 is estimated to be $5 \times 10^{-12}\ cm^3$ $molecule^{-1}\ sec^{-1}$, or $3 \times 10^9\ l\ mol^{-1}\ sec^{-1}$. This is close to the value of k_2 derived from a least squares fit of the long tail of figure 9b (30 µsec < t < 500 µsec) to a second order rate law with reactants of equal concentration

$$\frac{1}{A_t} = k_2' t + \frac{1}{A_o}$$

which gave $k_2' = (4.5 \pm 0.4)\ 10^8\ \mathrm{sec}^{-1}$. This constant is related to k_2 by $k_2 = \varepsilon\, l\, k_2'$ (ε is the infrared extinction coefficient of the 1847 cm^{-1} C=O stretch absorption, l is the optical pathlength). The extinction coefficient of the carbonyl CO mode is of the order of 100 $\mathrm{l\ mol}^{-1}\ \mathrm{cm}^{-1}$, and the thickness of the zeolite wafer is 100μ. Hence, ε l is around 1 $\mathrm{l\ mol}^{-1}\mathrm{cm}^{-1}$, and the fit of the experimental data gives $k_2 = 5 \times 10^8\ \mathrm{l\ mol}^{-1}\ \mathrm{sec}^{-1}$. This is close to the collision-controlled value predicted by the model for nongeminate encounters. We conclude that the two observed components of the HCO decay coincide with the predicted kinetics for geminate and nongeminate reaction of HCO with CH_2OH radicals. Clearly, the random walk model furnishes an understanding of the rate of the radical decay in the zeolite environment.

4.1.2 Transient CH_3CO Radical in NaY

There are striking similarities as well as differences between the kinetic behavior of the HCO and CH_3CO radicals in the same NaY zeolite environment. The acetyl radicals were produced by photodissociation of two different precursors, namely pinacolone (CH_3-C(=O)-C(CH_3)$_3$) or 1-naphythyl acetate (CH_3-C(=O)-$OC_{10}H_7$) [68,69]. Step-scan FT-IR runs at 5 μsec resolution using 8 nsec UV laser pulses revealed the same transient absorption at 2127 cm^{-1} for all precursors, as shown in the top part of figures 11 and 12. Despite the large blue shift compared to HCO radical, or CH_3CO radical in solution or rare gas matrix [70,71], the band can confidently be assigned to a CO stretching mode by virtue of the observed ^{13}C isotope shift of 34 cm^{-1} (figure 12a). The only alternative possibility to acetyl radical assignment is the corresponding cation, $CH_3C{=}O^+$, whose absorption in solution is around 2200 cm^{-1} [72]. However, recent ab initio calculations on the interaction of the an acyl radical with a small cation (hydronium ion)[73] predict a blue shift of the CO stretch by 220 cm^{-1}, which is close to the observed shift for CH_3CO in NaY. Hence, the very large shift can be explained by interaction of the lone pair electrons on the oxygen with the unshielded Na^+ ions in the supercage. As electron charge is transferred from the oxygen lone pair toward the sodium, electron density is pulled from the highest, singly occupied molecular orbital (lone electron on carbon) to the oxygen lone pair orbital [68]. This results in a partial triple CO bond in the case of CH_3CO, but not for HCO. A second factor that favors the assignment of the 2127 cm^{-1} absorption to an acetyl radical rather than an acetylium ion is the poor electron affinity of *t*-butyl radical; the formation of an ion pair upon dissociation of pinacolone is energetically very unfavorable.

Like HCO, the acetyl radicals survive on the microsecond time scale at room temperature. This suggests that the radical pairs generated by photodissociation of the precursor separate quantitatively, which seems to be a typical behavior of radical pairs in zeolite Y rather than an exception. At the same time, there is an important difference in the decay kinetics of formyl radical and acetyl radical in that no second order component is observed for CH_3CO no matter which precursor is chosen. In fact, the acetyl radical decay is best described by a single exponential law with a 1/e time of 71 μsec (1-naphthyl acetate precursor), or 315 μsec (pinacolone). Assuming the decay of the radical, as in the case of HCO, is dictated by random walk following separation from the supercage in which photolysis took place, the absence of a flat tail implies that the radicals are not subject to nongeminate encounters. This indicates that the radical fragments of photolyzed precursor are unable to diffuse sufficiently far to penetrate the diffusion sphere of a neighboring radical pair. We believe that the main factor responsible for the much shorter diffusion range in the acetyl radical systems is the low mobility of the relatively bulky 1-naphthyl acetate or pinacolone precursor [69]. Pinacolone and naphthyl acetate are considerably more bulky and therefore much less mobile than acetyl radical. The concentration of precursor molecules is typically about one per supercage, which is many orders of magnitude higher than that of the transient. This means that the randomly hopping radicals are not able to diffuse through the entire zeolite crystallite. Rather, their path is restricted to a subspace of the zeolite crystallite as the more abundant and slowly diffusing precursor molecules block window openings and obstruct passage through supercages. A similar percolation effect was experimentally observed for the highly mobile methane in zeolite NaY when co-loaded with much more slowly diffusing benzene molecules [62,74]. As a result, the random walking radicals are prevented from exploring the entire volume of the zeolite and are confined to pockets that are sufficiently small as to not intersect [69]. This explanation agrees with the observed single exponential decay characteristic of a geminate radical reaction.

The step-scan FT-IR studies of CH_3CO and HCO constitute the first detection of small transient radicals in a zeolite by any technique. Because of the wide spectal range of FT-IR spectroscopy and the fact that many catalyst supports are transparent throughout a considerable part of the infrared region, this method opens up mechanistic studies of reactions on porous supports at a new level of detail.

4.2 Mechanism of Redox Chemistry in Photo-Activated Transition Metal Sieves

Microporous or mesoporous materials containing transition metal centers as part of the framework, or grafted onto the pore surface constitute a new class of catalytic materials. Among the microporous sieves, these are typically framework substituted silicates [75,76], aluminophosphates, or silicoaluminophosphates [77,78]. With the recent discovery of mesoporous silicates with large, tens of Angstroms pore diameter [79], covalent anchoring (grafting) of transition metal centers on the inner surface became feasible [80-82], in addition to isomorphous framework substitution already used earlier for microporous sieves [83,84]. The first and best-known framework substituted metal sieve is Ti silicalite (TS-1) discovered by the Enichem group in 1983 [85,86]. The material has already found commercial application as a selective oxidation catalyst using hydrogenperoxide as oxidant [75]. With the vigorous search for new types of transition metal sieves now underway, there is no doubt that new useful catalysts will emerge. Elucidation of the elementary steps upon interaction of reactants with the metal centers by time-resolved FT-IR spectroscopy offers the most direct way of probing the redox reactivity of these new materials.

Among the metals of most interest in catalysis, iron is of particular importance because of its redox properties and abundance. Fe aluminophosphate sieve $FeAlPO_4$-5 (abbreviated FAPO-5) is a robust microporous material of AFI structure in which about one percent of the Al or P centers are isomorphously substituted by Fe, as illustrated in figure 13 [87]. The sieve consists of a one-dimensional system of 7.3 Å diameter channels with a pore volume of 0.18 cm^3g^{-1} [87-89]. Since Al and P are tetrahedrally coordinated, Fe is forced by the framework into tetrahedral coordination as well. This makes the metal centers at the pore surface readily accessible for interaction with adsorbed molecules. After synthesis of FAPO-5, Fe is in the oxidation state +III. The material may exhibit spontaneous redox reactivity by activation of the Fe by reducing it to Fe^{+II}. In fact, such activation can be accomplished by excitation of an optical absorption in the blue and near –UV region, shown in figure 14, because the transition involves transfer of an electron from framework oxygen to Fe^{+III} (ligand-to-metal charge-transfer (LMCT) transition)

$$Fe^{+III} - O^{-II} \xrightarrow[\text{LMCT}]{} Fe^{+II} - O^{-I}$$

This opens up opportunities for triggering redox chemistry of adsorbed molecules and monitoring elementary reaction steps by time-resolved FT-IR spectroscopy.

O_2 and CH_3OH have well-established redox potentials, which make them useful for probing the redox properties of framework metal centers at the gas-micropore interface. Oxygen, in particular, is an ideal acceptor for probing the reducing power of a catalyst because its redox potential is nearly independent of the environment in which it reacts [90]. We have employed both rapid-scan and step-scan FT-IR spectroscopy to elucidate the mechanism of $CH_3OH + O_2$ redox reaction at photo-activated Fe centers of FAPO-5 sieve [91]. Preliminary static difference FT-IR spectra recorded upon excitation of the LMCT absorption for 30 min. or longer revealed only 4-electron transfer products HCO_2H (most of it present as formate ion), H_2O, and HCO_2CH_3 (methyl formate) [63]. The latter emerged from a secondary thermal reaction, namely condensation of formic acid product with excess methanol. As can be seen from the rapid-scan spectra for the $CD_3OD + O_2$ case, shown in figure 15, formate (DCO_2^-, 1615

cm^{-1}) grows in according to a first order rate law with a rise time of 4 sec (250 K). The reaction with D-labeled methanol is shown here because, for this isotopic modification, the desorption-induced changes of the intense methanol bands lie outside the 2000-1300 cm^{-1} region and therefore do not interfere with the product growth measurement [91].

4.2.1 Rapid Scan Results

The rapid scan runs consisted of the recording of 99 interferograms over a period of 12.8 sec, each of 128 msec duration, after initiation of reaction by an 8 nsec 355 nm laser excitation pulse (a double-sided interferogram each during forward and backward motion of the mirror, 4 cm^{-1} resolution). Ten consecutive interferograms were automatically averaged during acquisition of the initial 50 interferograms, furnishing 5 averaged interferograms of 1.28 sec resolution. The following 40 interferograms were all averaged to yield a single time slice of 5.1 sec duration. This is justified by the fact that it encompasses the slow portion of the kinetics, and greatly simplifies the analysis. The remaining 9 interferograms were averaged and constitute the last data point before initiating the reaction again with a fresh laser pulse. Hence, the data obtained after each initiation pulse consist of 7 averaged interferograms, resulting in 7 single beam spectra upon Fourier transformation with midpoints at 0.6, 1.9, 3.2, 4.5, 5.8, 9.0, and 12.2 sec after triggering. Each rapid-scan experiment comprised the result of 50 laser pulses, leading to a 50x7 matrix of single beam spectra (see figure 1). The traces of figure 15 for each time delay were obtained by ratioing each of the 50 corresponding single beam spectra (one of the 7 averages after each pulse). These 50 ratioed spectra were then averaged to yield the absorbance time slice for a given delay. The small signal (on the order of 10^{-5} absorbance units for the formate band) required averaging of the results of 10 such rapid-scan experiments.

Since the rise of formate and H_2O is on the order of seconds, the signal-to-noise ratio of the rapid-scan experiments could be improved by exciting the Fe centers over a longer period of time. Figure 16a shows the results of a rapid-scan experiment of the parent $CH_3OH + O_2$ reaction on the second time scale, using the same data acquisition protocol just described (figure 15) except that the Fe was activated by a train of 10 consecutive laser pulses (one 8 nsec pulse per 100 msec, total duration 1 sec) instead of just one pulse. The times indicated in the figure refer to the time elapsed after completion of the photolysis period. The strong bleach in the 1500-1300 cm^{-1} region is due to consumption of CH_3OH by reaction as well as partial desorption by the laser-induced temperature rise of a few degrees. The contribution of physical desorption is confirmed by a rapid-scan experiment using CH_3OH and N_2 instead of O_2, shown in figure 16b. There is no product growth in this case, yet substantial transient desorption of methanol, which readsorbs completely within 10 seconds. As expected, the intensity of the $CH_3OH + O_2$ product bands of figure 16a exceeds that of the single pulse experiment by about a factor of ten. On the other hand, the transient spectra look different from those recorded after a single excitation pulse. Aside from a small amount of $CH_2{=}O$ observed at 1726 cm^{-1}, the spectra recorded just after initiation of reaction are dominated by HCO_2H (1679 cm^{-1}) and H_2O (1650 cm^{-1}). These assignments were confirmed by observation of $H^{13}CO_2H$ (1638 cm^{-1}) and DCO_2H (1660 cm^{-1}) when conducting experiments with the corresponding isotopically labeled methanol samples [91]. The evolution of the spectra shows that formic acid converts to formate (HCO_2^-, 1625 cm^{-1}) within 10 sec, consistent with the results of the static FT-IR work. The instantaneous appearance of HCO_2H + H_2O when exciting the sample with 10 laser pulses, but not when using a single pulse implies that these are secondary photolysis products of an intermediate that is generated on a time scale short compared to the photolysis period (1sec). A comprehensive study of all possible intermediates that could serve as precursors of HCO_2H and H_2O in FAPO-5 sieve revealed HO_2CH_2OH as the only candidate with the appropriate thermal and photochemical properties [92].

4.2.2 Step-Scan Results

To obtain direct evidence for the intermediacy of HO_2CH_2OH, step-scan FT-IR measurements of the CH_3OH + O_2 reaction in FAPO-5 were conducted at 5 μsec resolution. A transient absorption was detected at 1455 cm^{-1} that coincides with the sole infrared band of HO_2CH_2OH in the 2500-1300 cm^{-1} region in which step-scan measurements in FAPO-5 sieve can be conducted with sufficient sensitivity (two CH stretching absorptions of HO_2CH_2OH at 2884 and 2948 cm^{-1} are in a region where the noise is to high for step-scan measurements because of scattering). The assignment of the transient band, shown in figure 17a upon averaging over 500 μsec, is based on comparison with the infrared spectrum of an authentic hydroxymethyl hydroperoxide sample loaded into FAPO-5 [92]. The finding that HO_2CH_2OH grows in on the μsec time scale rules out the possibility that it is produced by any process other than direct coupling of HOO and CH_2OH radicals. The only alternative, namely reaction of CH_2=O and H_2O_2 is ruled out by our observation of a 2.6 sec reaction time (250 K) [91]. Moreover, a shorter lived transient with a maximum at 2204 cm^{-1} was observed in the case of the CD_3OD + O_2 reaction, shown in figure 17b upon averaging over 50 μsec. The species decays on the hundreds of μsec time scale and is attributed to the hydroxymethyl radical (CD_2OD) that precedes the formation of hydroxymethyl hydroperoxide.

These time-resolved FT-IR results allow us to propose the detailed mechanism for reaction of CH_3OH and O_2 with activated Fe centers shown in figure 18.

Fe^{+III}-O^{-II} $\longrightarrow$ Fe^{+II}-O^{-I} excitation results in transiently reduced Fe centers and a hole on a framework oxygen. The initial electron-transfer steps are reduction of O_2 by Fe^{+II} to O_2^- and concurrent oxidation of CH_3OH by the election-deficient framework O to methanol radical cation. The highly acidic CH_3OH^+ is expected to undergo efficient proton transfer to superoxide to form HOO and CH_3O radical. The latter is unstable relative to CH_2OH, and isomerization to CH_2OH is known to be extremely fast [91]. HOO and CH_2OH couple on the μsec timescale to yield the 2-electron-transfer product HO_2CH_2OH, which spontaneously rearranges to HCO_2^- and H_2O within 4 sec (250 K).

An important implication of this mechanism is that O_2 acts as one-electron acceptor, that is, the transient Fe^{+II} centers are capable of reducing O_2 in a thermoneutral or exoergic step. It means that the reduction potential of framework Fe^{+II} is equal or more negative than the standard potential for one-electron reduction of O_2, which is –0.33V versus NHE [90]. This is more than 0.6V more negative than the reduction potential of the conduction band electrons of dense-phase Fe_2O_3 semiconductor particles (0.3V) [93]. It suggests that the reduced framework Fe centers of the sieve have substantially stronger reducing power that the Fe_2O_3 conduction band electrons. We believe that this reflects the less stable tetrahedral coordination into which Fe centers are forced by the aluminophosphate framework. Iron in the +II oxidation state prefers octahedral coordination [94], and loss of stability of Fe^{+II} will increase the reducing strength of the metal. The shift toward more negative reduction potential of reduced FAPO-5 sieve compared to band-gap activated Fe_2O_3 may open up demanding reductions, e.g. of carbon oxides that are not accessible with iron oxide semiconductor materials. Substantial change of the redox properties by an unusual coordination imposed by the framework on the transition metal center is one of the unique aspects of porous transition metal catalysts.

5. Conclusions

The recent work by several groups using pulsed release of reactants coupled with rapid-scan FT-IR spectroscopy on the second or hundreds of millisecond time scale demonstrates that detection of reaction intermediates of heterogeneous catalysis in a time-resolved mode, even at modest resolution, furnishes new mechanistic information not accessible under steady state conditions. Given that the current time limit of rapid-scan spectrometers is considerably better than that (about 10 milliseconds), and pulsed mechanical valves with submillisecond response are now available, a wider use of this readily accessible method has the potential of substantially improving the mechanistic understanding of a variety of heterogeneous catalytic systems under reaction conditions.

The capability of detecting small transient radicals on heterogeneous catalysts made possible by the step-scan FT-IR technique opens up the study of primary steps under reaction conditions. Direct observation of early elementary events of catalysis is expected to reveal the key intermediates that steer the reaction towards final products. Understanding of the detailed reaction path offers opportunities for influencing product selectivity, which makes the application of this technique in mechanistic studies of heterogeneous catalysis particularly useful. While microsecond resolution appears to be adequate for the monitoring of even small transient radicals on zeolite supports due to their high mobility in the pore network, the full capability of 10 nanoseconds resolution may become important when studying catalysts involving other types of supports. Ten nanosecond step-scan absorption spectroscopy is now well established for reactions in homogeneous media or photophysical processes in solids, but further improvement of the sensitivity is needed for work on chemical reactions in heterogeneous environments at this time limit.

While developed thus far primarily for mechanistic studies of photocatalytic systems in micro or mesoporous materials, the step-scan method is equally applicable in principle for thermal catalytic reactions. It requires photo-triggered release of a reactant by a nanosecond pulse from a precursor, such as a transition metal complex featuring the reactant as a ligand, in the immediate proximity of the catalyst. In certain cases, even ultrafast timescales may be required in order to access the primary events. In fact, following initial experiments by Heilweil et al. [95,96], the groups of Hirose and van Santen have recently demonstrated the use of ultrafast infrared laser techniques on acid zeolite catalysts by probing the vibrational or conformational dynamics of Bronsted acid sites and of adsorbed reactants [97,98].

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Figure Captions

Figure 1: Principle of the rapid-scan FT-IR method. The arrow indicates pulsed initiation of chemical reaction.

Figure 2: Principle of step-scan FT-IR spectroscopy. Adapted from Ref. 17, W. Uhmann et al., *Appl. Spectrosc.* **45**, 390 (1991).

Figure 3: Infrared spectral changes upon release of a pulse of NO gas into a steady flow of CO (in He) over an SiO_2-supported Rh catalyst at 473 K. From Ref. 43, R. Krishnamurthy et al., *J. Phys. Chem.* **99**, 16727 (1995).

Figure 4: Rapid-scan FT-IR spectra following adsorption of ^{14}NO gas onto Co^{2+}-exchanged ZSM-5 zeolite containing preadsorbed ^{15}NO. (a) After exposure of the catalyst to 13 Torr ^{15}NO for 120 min followed by evacuation at room temperature. (b) after 0.3 sec following admission of 13 Torr of ^{14}NO. (c) after 0.4 sec. (d) 0.5 sec. (e) 0.7 sec. (f) 5.0 sec. (g) 3.0 min. From Ref. 32, M. Iwamoto et al., *Chem. Lett.*, 729 (1995).

Figure 5: Supercage of zeolite Y (13 A diameter) with four windows (8 A) interconnecting adjacent cages. Adapted from Ref. 88, W.M. Meier et al., *Zeolites* **17**, 26 (1996).

Figure 6: (a) FT-IR spectrum of glycolaldehyde adsorbed onto dehydrated NaY zeolite. (b) Difference spectrum upon 15 min irradiation at 266 nm at 4.2 mJ cm^{-2} $pulse^{-1}$ (10 Hz).

Figure 7: FT-IR difference spectrum of glycolaldehyde photolysis following 15 min irradiation at 266 nm, recorded at 0.25 cm^{-1} resolution.

Figure 8: Reaction pathways leading to observed products upon glycolaldehyde photodissociation in zeolite NaY.

Figure 9: (a) Step-scan FT-IR spectra of glycolaldehyde photodissociation initiated by 266 nm laser pulses of 8 nsec duration at room temperature. The time resolution is 5 μsec. (b) Decay of the 1847 cm^{-1} transient.

Figure 10: (a) Step-scan FT-IR spectra of acetaldehyde and acetaldehyde-$^{13}C_2$ photodissociation by 290 nm laser pulses of 8 nsec duration at room temperature. The spectra were recorded at 25 nsec resolution and represent the coaddition of 200 timeslices over the first 5 μsec after the photolysis pulse. (b) Decay of the 1845 cm^{-1} transient.

Figure 11: (a) Step-scan FT-IR spectra of pinacolone photodissociation by 290 nm laser pulses at room temperature. The solid trace represents the 50 μsec average recorded by coaddition of ten 5 μsec timeslices, the dotted trace is the coaddition

of ten timeslices in the 250-300 μsec range. (b) Decay of the 2127 cm^{-1} transient. The solid curve represents a fit to a single exponential law.

Figure 12: (a) Step-san FT-IR spectra of 1-naphthyl acetate photodissociation with 308 nm pulses of 8 nsec duration at room temperature. The traces correspond to the coaddition of ten timeslices recorded at 5 μsec resolution. The top traces show the transient when using a precursor with a ^{13}C-labeled carbonyl group. (b) Decay of the transient. The solid curve represents a fit to a single exponential law.

Figure 13: Isomorphous framework substitution of Fe in $AlPO_4$-5 (AFI) sieve. Adapted from Ref. 88, W.M. Meier et al., *Zeolites* **17**, 26 (1996).

Figure 14: Diffuse reflectance spectrum of FAPO-5 molecular sieve showing the ligand-to-metal charge-transfer transition (LMCT) used to activate the Fe centers.

Figure 15: (a) Rapid-scan FT-IR spectra of single pulse-induced $CD_3OD + O_2$ photoreaction in a FAPO-5 sieve at 250 K recorded at 1.9, 3.2, 4.5, 5.8, 9.0, and 12.2 sec after the 355 nm excitation pulse. Alternate traces are dashed for clarity. (b) Single exponential fit of the absorbance growth.

Figure 16: (a) Rapid-scan FT-IR spectra of 355 nm induced $CH_3OH + O_2$ reaction in a FAPO-5 sieve at 250 K. Spectra were recorded on the sec time scale following

excitation of the sample for 1.1 sec by a sequence of 355 nm pulses at 10 Hz. Dotted trace is a spectrum recorded during laser irradiation. (b) Result of identical experiment for the $CH_3OH + N_2$ system.

Figure 17: (a) Step-scan FT-IR spectrum of $CH_3OH + O_2$ photoreaction in a FAPO-5 sieve at 250 K. One hundred timeslices of 5 µsec resolution were coadded. An identical experiment for $CH_3OH + N_2$ is shown, which was subtracted from the $CH_3OH + O_2$ spectrum to obtain a transient spectrum free of methanol desorption due to slight sample heating (one degree) by the laser pulse (insert). (b) Step-scan spectrum of $CD_3OD + O_2$ photoreaction in FAPO-5 representing ten coadded timeslices at 5 µsec resolution.

Figure 18: Proposed mechanism for $CH_3OH + O_2$ redox reaction at excited Fe framework centers of FAPO-5 sieve.